# MODEL EVALUATION OF DRY DEPOSITION TO VEGETATION FOR VOLATILE AND SEMI-VOLATILE ORGANIC COMPOUNDS IN A MULTIMEDIA ENVIRONMENT*

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**Abstract.** Gas-phase atmospheric deposition was evaluated in a screening level model of the multimedia environmental distribution of toxics (MEND-TOX). Algorithmic additions to MEND-TOX for the estimation of gas-phase deposition velocity over vegetated surfaces were analyzed using recently published dry deposition flux measurements for nitric acid. Model outputs are compared to similar estimates from the NOAA multilayer dry deposition model. Results of the evaluation indicate that MEND-TOX performs well as a screening level model for the estimation of gas-phase dry deposition velocity of nitric acid over soybeans. The present study expands previous laboratory results for organic species to include an inorganic species and open field and dry leaf, conditions.

**Keywords:** gas-phase deposition, multimedia, nitric acid, screening model, vegetation

## 1. Introduction

Pollutants that are released to the environment are known to migrate across phase boundaries. As a consequence, pollutants are distributed throughout the multimedia environment. Clearly, understanding the environmental impact of pollutants requires understanding their environmental multimedia distribution and intermedia transport.

The exchange of pollutants between the atmosphere and vegetation, which is the subject of the present study, is one example of intermedia exchange in a multimedia environment.

There are four major multimedia modelling approaches. Integrated spatial multimedia models are those models in which all media are described *via* spatial models, interactions take place through well-posed boundary conditions and all equations are solved simultaneously for the interacting system. Linked multimedia models consist of linked single-medium models for the air, water, soil, water, and other environmental compartments of interest. Compartmental models are

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essentially mass balance models in which the concentration in each medium is assumed to be 'well-mixed'. Finally, integrated spatial-multimedia-compartmental models (ISMCM) belong to a class of multimedia models that include both 'well-mixed' compartments and spatial compartments tightly integrated through well-posed physical boundary conditions.

All four modelling approaches have evolved significantly over time to reflect changing environmental concerns and the current state of scientific knowledge. The present study evaluates the treatment of gas-phase atmospheric deposition in the Multimedia Environmental Distribution of Toxics (MEND-TOX) model, a recent addition to the screening level ISMCM-family. We briefly describe the model, focusing on algorithms to estimate gas-phase deposition velocity over vegetated surfaces. MEND-TOX deposition velocity predictions are then evaluated in light of recently published dry deposition flux measurements and compared to similar estimates produced by the NOAA multilayer dry deposition model (MLM) (Meyers *et al.*, 1998). We conclude with suggestions for further model improvement and areas in need of additional basic research or field monitoring efforts.

## 2. The Multimedia Model

MEND-TOX is part of the ISMC family of models previously used to evaluate the partitioning of PCBs, PAHs and TCE in California (Cohen and Clay, 1994; Tsai, *et al.*, 1991; Cohen, 1996; Ryan and Cohen, 1985), the Great Lakes (Vohra, 1996) and the Southeast Ohio River Valley (Ryan and Cohen, 1986). Like these earlier models, MEND-TOX tracks the dynamic distribution of chemicals in a multimedia setting based on a detailed mechanistic description of intermedia transfer processes. It describes environmental media in terms of eight major compartments: air, aerosol, soil, water, sediment, suspended solids, biota, and vegetation. Atmospheric (aerosol and gas), vegetation and aquatic (i.e., water, biota, and suspended solids) compartments are treated as well-mixed (i.e., uniform) and the chemical mass balance in these compartments is expressed *via* ordinary differential equations. The soil and sediment compartments are taken to be non-uniform, and transport is described by one-dimensional convective-diffusion-reaction equations.

Modules to predict precipitation scavenging of gases, infiltration of dissolved solutes into the soil and sediment, intermedia transfer of particle-bound chemicals by dry and wet deposition, wind resuspension and sediment resuspension and deposition are included in MEND-TOX. The basic output from MEND-TOX is in the form of concentrations as a function of time for the uniform compartments and time-dependent spatial concentration profiles for the non-uniform compartments (i.e., soil and sediment). Model output also includes the mass distribution of the chemical in the multimedia environment as well as the time-dependent intermedia mass fluxes. MEND-TOX addresses atmospheric deposition of organic chemicals to water, soil and vegetation media. Chemical exchange across any media boundary utilizes a traditional two-film theory approach expressed as

$$N = K_G(C_g - HC_c) = -K_x(C_x - C_g/H) \tag{1}$$

where $K_G$ (cm s$^{-1}$) and $K_x$ (cm s$^{-1}$) are the overall mass transfer coefficients (MTC) between the gas phase of the chemical in the atmosphere and some adjoining medium, $X$ (e.g., soil, water, vegetation), and $N$ is the interfacial mass flux between the two media (g cm$^{-2}$ s$^{-1}$). $H$ is a dimensionless Henry's Law-type constant which acts as a partitioning coefficient between the air and the adjacent media. Gas-phase concentrations of the chemical in air and in an adjacent medium (e.g., vegetation) are represented by $C_g$ and $C_x$, respectively. It is assumed that the interfacial concentrations are at equilibrium. The values of the MTCs depend on the prevailing turbulence levels in the two media, media temperature, the properties of the solute such as diffusivity, or molecular size and, in some cases, media geometry (Cohen, 1996). MEND-TOX treatment of the transfer of atmospheric particles and gases to soil and liquid surfaces is described elsewhere (Tsai *et al.*, 1991; Vohra, 1996). The present analysis focuses only on the recent addition of algorithms for the estimation of gas-phase mass transfer from the atmosphere to a vegetated surface. A brief description of these algorithms follows.

Paterson *et al.* (1991) apply a conventional two-compartment chemical kinetic uptake-clearance approach, defining the overall air to leaf mass transfer coefficient (MTC), $K_{OAL}$ (m h$^{-1}$) as

$$K_{OAL} = \left(\frac{V}{A}\right) k_1 = \left(\frac{V}{A}\right)\left(\frac{k_2}{H_{AL}}\right) \tag{2}$$

with,

$$\frac{1}{k_1} = H_{AL}(\tau_O + K_{OA}\tau_A) \tag{3}$$

where $k_1$ and $k_2$ are uptake and clearance rate constants (h$^{-1}$), $V$ is vegetation volume (m$^3$), $A$ is vegetation area (m$^2$), $H_{AL}$ is the air/leaf partition coefficient (dimensionless), $\tau_O$ (hr) is an organic phase chemical transfer time, $\tau_A$ (hr) is an air transfer time and $K_{OA}$ is the octanol-air partition coefficient.

Equation (3) implies that air and organic resistance are in series and can be estimated as

$$\tau_O = \frac{V y_o}{K_C A} \tag{4}$$

and,

$$\tau_A = \frac{V y_o}{K_A A} \tag{5}$$

where $y_o$ is the mass fraction of octanol in the plant, $K_C$ (m $h^{-1}$) is the MTC for the plant cuticle and $K_A$ (m $h^{-1}$) is the MTC for the air boundary layer. Octanol is frequently used as a surrogate for lipids (fats) so that $y_O$ represents the lipid fraction of the plant mass. Equation (3) assumes that the primary site of chemical accumulation is in the cuticular waxes, which are similar to octanol in partitioning properties.

Paterson *et al.* (1991) tested these relationships for 14 organic compounds in a laboratory setting. Their results indicate that when $\log(K_{OA})$ is less than 7, $\tau_O$ is much larger than $K_{OA}\tau_A$ and organic resistance dominates the estimation of $V_d$. When $\log(K_{OA})$ is approximately equal to 7, $\tau_O$ and $K_{OA}\tau_A$ are of similar magnitude. When $\log(K_{OA})$ is greater than 8, $K_{OA}\tau_A$ becomes much larger than $\tau_O$ and atmospheric resistance controls the $V_d$ estimate.

Estimates of $\tau_O$ and $\tau_A$ are needed to evaluate Equation (3). While $\tau_A$ can be easily approximated (see Section 3.2), $\tau_O$ requires cuticular resistance information. Development of a numerical model for $\tau_O$ is undergoing research. Until such a model is identified and can be added to MEND-TOX, a fixed value of $\tau_O$ is employed and the model applied only in cases in which $\log(K_{OA})$ is large.

Soil surface and aerodynamic resistances can also be important factors for the estimation of gas-phase deposition velocity (Sauer *et al.*, 1995). Based on data reported in Lee *et al.* (1992), soil resistance for $HNO_3$ is estimated to be 30 s $m^{-1}$ (Meyers *et al.*, 1998). Cooter and Schwede (2000) estimate soil surface aerodynamic resistance and canopy resistance for $HNO_3$ and soybeans to be 50 to 75 s $m^{-1}$ and 10 to 15 s $m^{-1}$ respectively. Since the impact of combined soil factors, treated as parallel resistances by Meyers *et al.* (1998), on $HNO_3$ deposition velocity, $V_d$, are an order of magnitude less than those of canopy resistance, we assume here that $V_d$ is roughly equivalent to $K_{OAL}$.

## 3. Model Evaluation

Although MEND-TOX algorithms for chemical partitioning and particle deposition of PCBs, PAHs and TCE in several geographic settings have been verified (see previous references), similar field studies for gas-phase deposition to vegetation have yet to be reported. One reason for this absence is a lack of suitably detailed organic flux data. Lacking such information, two alternatives for evaluating the MEND-TOX algorithms are explored: selective use of available flux data for inorganic species and comparison of MEND-TOX estimates to those produced by alternative evaluated models.

### 3.1. OBSERVATIONS OF GAS-PHASE FLUX

Meyers *et al.* (1998) evaluate the performance of the MLM for inferring dry deposition velocity using an extensive flux monitoring data base. Pollutant fluxes and concentrations were measured from a mobile laboratory at various geographic locations. In one case, ozone ($O_3$), sulfur dioxide ($SO_2$) and nitric acid ($HNO_3$) were measured above soybeans near Nashville, Tennessee, during the summer and early fall of 1995.

At present, MEND-TOX is specifically designed to address the behavior of organic chemical species and so some mechanisms needed to adequately address inorganic chemical behavior in a multimedia environment are missing. In particular, MEND-TOX mechanisms do not address reactive inorganics in liquid solution. However, the Meyers *et al.* (1998) data base allows for preliminary verification studies for the intermedia transport process associated specifically with gas-phase deposition as long as (1) the gas-phase deposition is controlled primarily by atmospheric resistance factors, (2) deposition is primarily to the leaf cuticle, and (3) that the leaf surfaces are dry. Of the chemicals in the Meyers *et al.* (1998) data base, only $HNO_3$ meets the first two assumptions. All measurements taken over soybeans were made when leaves were dry and so the third assumption is met as well.

Meyers *et al.* (1998) report that soybeans (ASGROW 5560) were planted within wheat stubble on June 13, 1995. Dry deposition sampling was initiated on June 22. The beans went through a rapid growth period from July 10 to August 5 with the leaf area index (LAI, measured using a Licor 2000 plant canopy analyzer) increasing from 1 to about 6. LAI gradually decreased to about 3 by the end of September. By October 11, LAI decreased to about 1 when the beans were mostly stalks and pods.

MEND-TOX requires a number of plant- and soil-specific parameters before performing a full mass balance analysis. Since we intend to examine only those model elements that directly impact the estimation of gas-phase deposition velocity, parameter values for a 'typical' agricultural soil and soybean crop (e.g., organic carbon content, canopy height, etc.) are provided to the model. MEND-TOX is then provided with reported temperature, windspeed, estimates of leaf surface characteristics and $\tau_A$ for each 2-hr sampling period and a $K_{OAL}$, i.e., gas-phase $V_d$, estimate is produced. The process is repeated for each of the 39 valid observation periods.

## 3.2. MEND-TOX INPUT PARAMETERS

MEND-TOX inputs critical to the estimation of gas-phase $V_d$ over vegetation include fractions of lipid phase, water and air in the roots and foliage, leaf area, fresh above ground biomass, equilibrium partition coefficients (e.g., leaf-air) and values for $K_A$ and $K_C$.

The leaf/air equilibrium partition coefficient can be estimated by considering chemical partitioning to the leaf to be mainly due to the lipid, water and air phases of the leaf (Paterson *et al.*, 1991). This approach requires estimates of the fraction of air ($y_A$), water ($y_W$) and lipid ($y_O$) contained in the plant. A small, but non-zero value of 0.01 is assigned to $y_A$. Values for $y_W$ are allowed to range from 0.85 when plants are young or moisture plentiful to 0.15 at bean harvest. Wilkerson *et al.* (1983) suggest that a reasonable lipid fraction for soybean stem and leaf is about 0.03.

Daily plant biomass and leaf area were obtained *via* a U.S. Department of Agriculture simulation model, the Erosion Productivity Index Calculator (EPIC) (Williams *et al.*, 1984; Williams and Renard, 1985), previously employed to estimate LAI for input to the MLM (Cooter and Schwede, 2000). EPIC plant parameters were tuned so that model output matched the LAI and phenological information reported by Meyers *et al.* (1998). The surface area of foliage available to intercept the depositing gas is estimated as the ratio of leaf area to fresh leaf mass ($\mathrm{cm}^2\,\mathrm{gm}^{-1}$). The ratio of leaf volume to leaf area, $V/A$, can be approximated as the average leaf thickness for the plant. Laboratory studies suggest that a 'typical' leaf thickness for conventional soybeans ranges from 180 to 200 $\mu$m (Dr. James Dunphy, North Carolina State University Extension Soybean Specialist, personal communication).

Nitric acid has been selected to demonstrate a case in which precise estimation of variations of $\tau_O$ to environmental factors is not critical. A fixed value of $2.0 \times 10^{-11}$ (hr) suggested by the parameterizations described in Wesely (1989) is assigned to $\tau_O$ throughout the analysis.

A value for $\tau_A$ is computed for each sampling period in the $HNO_3$ data set. In this case, $K_A^{-1}$ is approximated as the sum of aerodynamic, $R_a$, and boundary layer, $R_b$, resistances. All $HNO_3$ observations were taken during daylight hours. Hicks *et al.* (1987) suggest that aerodynamic resistance ($R_a$) during daylight hours (unstable atmospheric conditions) can be computed as

$$R_a = \frac{9}{u\sigma_\theta^2} \tag{6}$$

where $u$ is the windspeed ($\mathrm{m\,s^{-1}}$) and $\sigma_\theta$ is the standard deviation of the wind direction, a surrogate for turbulence. Upon determination of $R_a$, an internally consistent value for the friction velocity, $u_*$ is obtained from the approximation

$$R_a \approx u u_*^{-2} \tag{7}$$

This procedure has been shown to provide very good estimates of $u_*$ for a wide range of atmospheric stabilities (Erisman and Duyzer, 1991). An estimate of $R_b$, conditioned on atmospheric stability, can then be estimated as

$$R_b = \frac{2}{ku_*} Sc^{2/3} \tag{8}$$

where $k$ is the Von Karman constant (0.4), and $Sc$ is the Schmidt number for $HNO_3$.

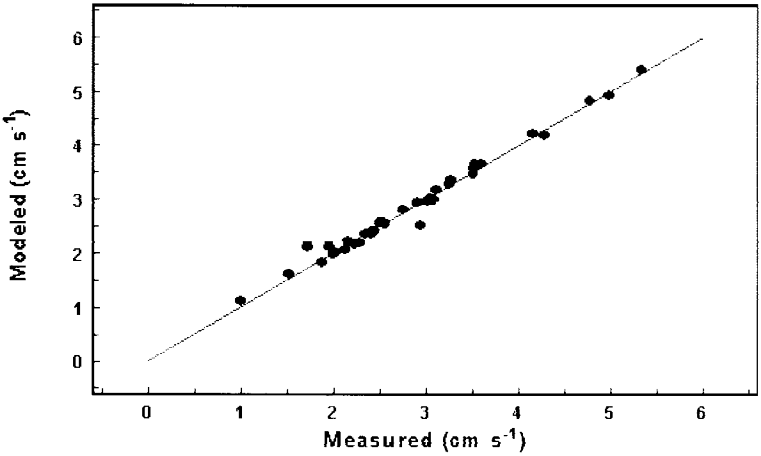

*Figure 1.* Modelled *vs* measured deposition velocities for $HNO_3$ over a soybean field near Nashville, TN.

TABLE I

Comparison of measured, MEND-TOX and NOAA gas-phase deposition velocity (cm $s^{-1}$) over a soybean field near Nashville, TN

| | Measured | MEND-TOX | MEND-TOX bias | NOAA-MLM bias |
|---|---|---|---|---|
| Number of measurements | 39 | 39 | 39 | 39 |
| Mean | 2.84 | 2.86 | –0.01 | 0.220 |
| Std. deviation | 0.941 | 1.060 | 0.117 | 1.010 |

## 4. Results and Discussion

An estimate of $K_{OAL}$ for each valid Meyers *et al.* (1998) $HNO_3$ observation was made as described in Section 3 and compared to observations (Figure 1). Summary statistics for the model estimates and observations are provided in Table I. Model bias is defined by Meyers *et al.* (1998) as (observed $V_d$ – model $V_d$). Model precision or random error is defined as $\sigma_{bias}$. These results suggest that MEND-TOX possesses a good overall gas-phase dry deposition velocity estimation capability for $HNO_3$ over soybean (i.e., bias and precision near 0).

Meyers *et al.* (1998) describe the performance of the NOAA-MLM model given the same meteorological data and plant conditions (LAI) used in the MEND-TOX analysis. Their results for soybeans, reported as model to observed bias, are provided in Table I. Meyers *et al.* (1998) conclude that the MLM showed good agreement in the mean $V_d$, with very small average bias. However, for specific periods the model either underpredicted or overpredicted $V_d$, leading to relatively low estimates of linear correlation (Dr. Peter Finkelstein, NOAA/ARL, personal communication) (see Figure 6g, Meyers *et al.*, 1998). Previous sensitivity analyses have determined that, for crops with a single LAI peak such as corn or soybeans, MLM $V_d$ estimates for $HNO_3$ respond little to intraannual patterns of LAI and estimate variability is driven almost exclusively by patterns of atmospheric resistance, i.e., windspeed and turbulence (Cooter and Schwede, 2000). Atmospheric resistance also plays a dominant role in MEND-TOX (see previous $K_a$ discussion), but this influence is moderated by overall chemical partitioning behavior which, in turn, is influenced by leaf thickness, plant lipid and water content and biomass. The results are $V_d$ estimates that appear to more closely echo natural patterns of diurnal and day-to-day variability contained in the observation data set.

## 5. Conclusions

This summary is not a full verification of the MEND-TOX dry deposition algorithms. Previous laboratory results (Paterson *et al.*, 1991) suggest the MEND-TOX estimates should be reasonable for certain groups of organic chemicals. Given that the stated model assumptions regarding chemical properties are met, the present study has expanded these results to include an inorganic species under open field, as opposed to controlled laboratory, and dry leaf conditions

The greatest strengths of the MEND-TOX model are its ease of use and applicability for a wide range of organic chemicals. Its limitations are its focus on organic chemicals and an inability to address fully the effects of stomatal and cuticular resistance on $V_d$. The latter represents a significant limitation for many organic and inorganic chemical species and, as our understanding of these processes improves, should be addressed in future model versions.

Although there are many modelling and monitoring studies of $O_3$, sulfur and nitrogen deposition to soil, water and vegetation surfaces, there are few studies similar in quality and scope to Meyers *et al.* (1998) for gas phase organic species. Monitoring for such chemicals is expensive, time consuming and difficult. It is only through such efforts, however, that we can realistically verify the utility of scientifically sound, inexpensive, widely applicable, models such as MEND-TOX for initial screening-level multimedia assessments of volatile and semi-volatile chemicals.

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